

**INVESTIGATION OF
SHREDDED PESTICIDE CONTAINERS
FOR RECYCLING POSSIBILITIES**

BY

**Materials and Testing Department
Alberta Research Council
for
Alberta Environment
Environmental Protection Services**

APRIL 18, 1990

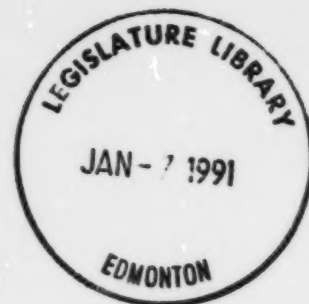


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EXECUTIVE SUMMARY

Samples of discarded plastic pesticide containers were examined for Alberta Environment to determine their recycling potential and to suggest possible products. The pesticide containers were analyzed for the following:

1. type of pesticide(s) and plastics present;
2. the presence of pesticides diffused into specific plastics samples;
3. the ability to remove residual pesticides by a washing technique; and
4. the effect of heating and extrusion of the cleaned and uncleaned plastic samples.

Testing revealed a wide range of pesticides present in the samples as received from Alberta Environment. Extrusion and heating of the pesticide-contaminated samples did not destroy the residual pesticides.

Washing the as-received pesticide container samples with detergent and water, methanol, or dichloromethane lowered the pesticide concentration, but did not remove the pesticides completely from the bulk sample. In most cases, even extensive washing or solvent extraction for extended periods followed by extrusion and rewashing the extrusion products, did not remove all of the pesticides.

The exact concentrations of the pesticides present in all the plastic samples were not determined. However, comparative or relative concentration levels for the pesticides detected in a particular extract were determined.

The direct measurement of the pesticides present in the plastic itself was done by mass spectrometric analysis of a very small portion of the plastic, using a solid probe technique. The results of the analysis indicate that certain pesticides are "dissolved" into the plastic and are not readily removed by surface washing. Solvent extraction over time indicates that these pesticides will diffuse from the plastic (on the twelfth day of a long-term extraction test 0.01% by weight of pesticide-containing samples was obtained). This suggests that dissolved or hard-to-remove pesticides present in the recycled plastic may result in a slow release of the pesticides from manufactured products.

Preliminary results of the testing (outlined below) were presented at a meeting of potential manufacturers of products made from the discarded pesticide containers. Also, information regarding the Alberta Research Council's Joint Research Venture program was provided. Using this program, interested applicants could obtain 50% of the funds for product development. As a result, several inquiries were received and one Joint Research Venture proposal is being actively pursued.

1. INTRODUCTION

1.1 Background

The prairie provinces' agricultural industries generate about 1.3 million kg of plastic pesticide containers per year. In Alberta, 250,000 kg/year of these containers are collected at designated sites throughout the province. There are approximately 450,000 kg of shredded containers presently stored at these sites. The containers are composed of mixed and unsorted plastics, and have various levels of contamination by pesticides and other foreign materials.

Alberta Environment is seeking a non-controversial solution to the problem presented by such accumulations of pesticide-contaminated plastic containers. Several possible solutions have been identified by the government. One solution being considered involves recycling the material into non-hazardous products that are both economical to produce and have a viable market. Alberta Environment would like to:

- have an independent evaluation done of the possible products created through this process;
- safe operating procedures by which to produce the products (i.e. cleaning and forming of the collected and shredded material);
- an assessment of the products as to their potential environmental hazards.

1.2 Project Objectives

To begin this evaluation, Alberta Environment contracted the Alberta Research Council to determine the feasibility of recycling pesticide-contaminated plastic containers. The ultimate objective is to have one or more companies manufacturing environmentally-acceptable products from the containers that are presently stockpiled.

The specific objectives of the project were to:

- identify the characteristics of the plastics and the types of pesticides present on the container samples as received from Alberta Environment.
- determine the ability to remove or deactivate the pesticide contaminants in ground plastic container samples.
- ascertain the types of pesticides that remain after various washing techniques and determine the most effective washing procedure.
- characterize the washed plastics for product applications.
- distribute the results of the materials characterization to interested participants.
- solicit in confidence, a list of possible products to be formed from the pesticide containers from interested manufacturers; evaluate the suggested products, and present this list to Alberta Environment.

2. CHARACTERISTICS OF THE SAMPLES

2.1 Experimental Results

Samples of shredded pesticide containers were provided by Alberta Environment. The samples were selected from materials which had been stockpiled at various locations throughout the province.

Five different samples labelled A, B, C, D, and E were delivered in tightly closed plastic bags and were immediately transferred to 20-liter plastic pails with airtight lids. The samples consisted of coarsely shredded plastic with the larger chunks being up to 5 cm wide and 12 cm long. Table 1 gives the respective weights of the samples as received.

2.2 Analysis of Samples

A large number of analytical results were collected. Only summary data are given here.

Samples were analyzed for pesticides by an extraction process followed by gas chromatography-mass spectroscopy (GC-MS). In this method a complex mixture is passed through a chromatographic column before flowing through a mass spectrometer. Different components are retained in the column for different amounts of time. Hence, the signal from the mass spectrometer as a function of time, such as that shown in Figure 1., can be interpreted as the relative concentrations of the various components.

The procedure involved the use of chloromethane to extract a representative portion of each of the samples. The samples were derivatized to make the pesticides, especially the organic acids, more volatile (see Appendix A). The advantage of this technique is that the most common pesticides can be analyzed in one run using this methodology. However, the results may not be quantitative. A portion of this modified extract solution was then injected into a gas chromatograph where the component pesticides were separated and identified using the mass spectrometer. The resulting chromatograms for each of the five individual samples are presented in Figure 1.

The original (i.e. unmodified) portions of the extracts were evaporated until a constant weight was reached at room temperature (20° C). It was observed that the amount of material extracted with dichloromethane varied slightly with each sample ranging from 1.2% to 2% of the original weight of shredded plastic sample.

The GC-MS analysis used for this study provides a qualitative analysis and confirms that the individual pesticides are present. The relative concentrations of the pesticides present in individual extracts was determined. However, no attempt was made to determine the absolute concentration of each of the identified pesticides as this was beyond the scope of the study. The areas under the peaks in the chromatograms give a semi-quantitative estimate of the concentration of individual pesticides relative to other pesticides in individual extracts. Absolute peak areas in different chromatograms cannot be compared because the samples were not identical.

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Table 1
Weight of Shredded Plastic Samples

<u>Sample</u>	<u>Weight in kg</u>
A Total A (1 bag)	5.50 (5.50)
B Total B (3 bags)	(wt/bag) (19.65)
C Total C (2 bags)	(wt/bag) (11.40)
D Total D (3 bags)	(wt/bag) (14.65)
E Total E (3 bags)	(wt/bag) (17.40 -----)
TOTAL SAMPLE WEIGHT	68.6

The average bulk density of the total sample was 0.29 kg/l.

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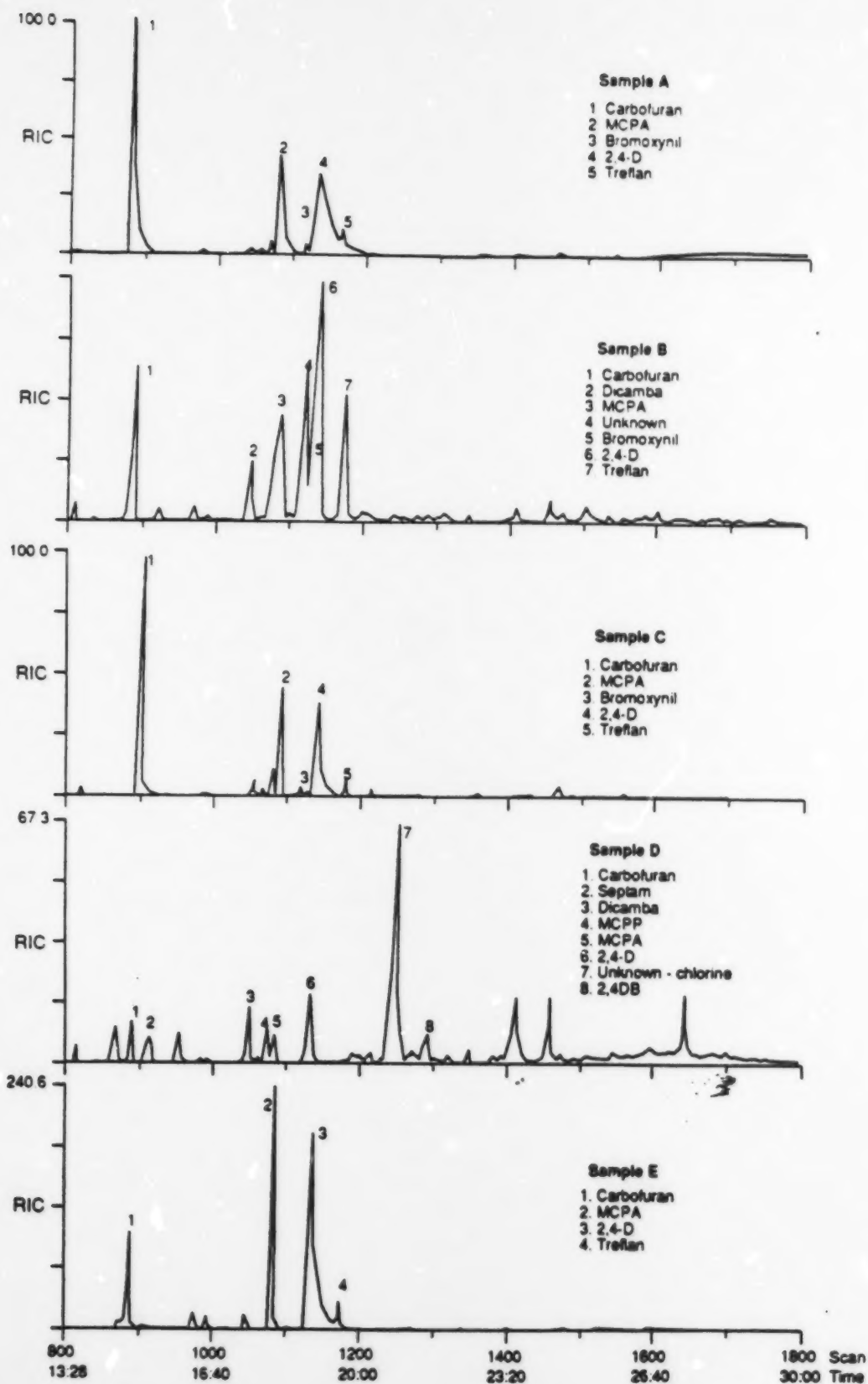


Figure 1. Pesticides chromatograms for as-received samples.
(Intensity (RIC) vs. Time)

A representative portion of each of the five samples was removed for chemical analysis, and the remainder blended to make a single composite sample. The composite sample was then pulverized to approximately 0.5 cm particles and reblended to provide a single homogeneous sample. The 60 kg pulverized composite sample had a bulk density of 0.32 kg/l unpacked and 0.37 packed.

A list of the pesticides that were identified in the individual samples appears in Table 2. A representative portion of the pulverized composite sample was extracted with dichloromethane and the pesticide content of the extract analyzed by GC-MS. The resulting chromatogram is shown in Figure 2A.

A portion of the pulverized composite sample (approximately 2 kg) was extruded through a 1 inch extruder fitted with a 1 X 0.3 cm die and a barrel temperature of 185 C. This "extrudate" was analyzed for pesticides by pulverizing it; extracting the pulverized sample with dichloromethane; and identifying the pesticides in the extract solution by GC-MS analysis. The GC results are shown in Figure 2B.

The chromatograms exhibit only small differences indicating that the extrusion process did not significantly change the distribution of the types of pesticides present.

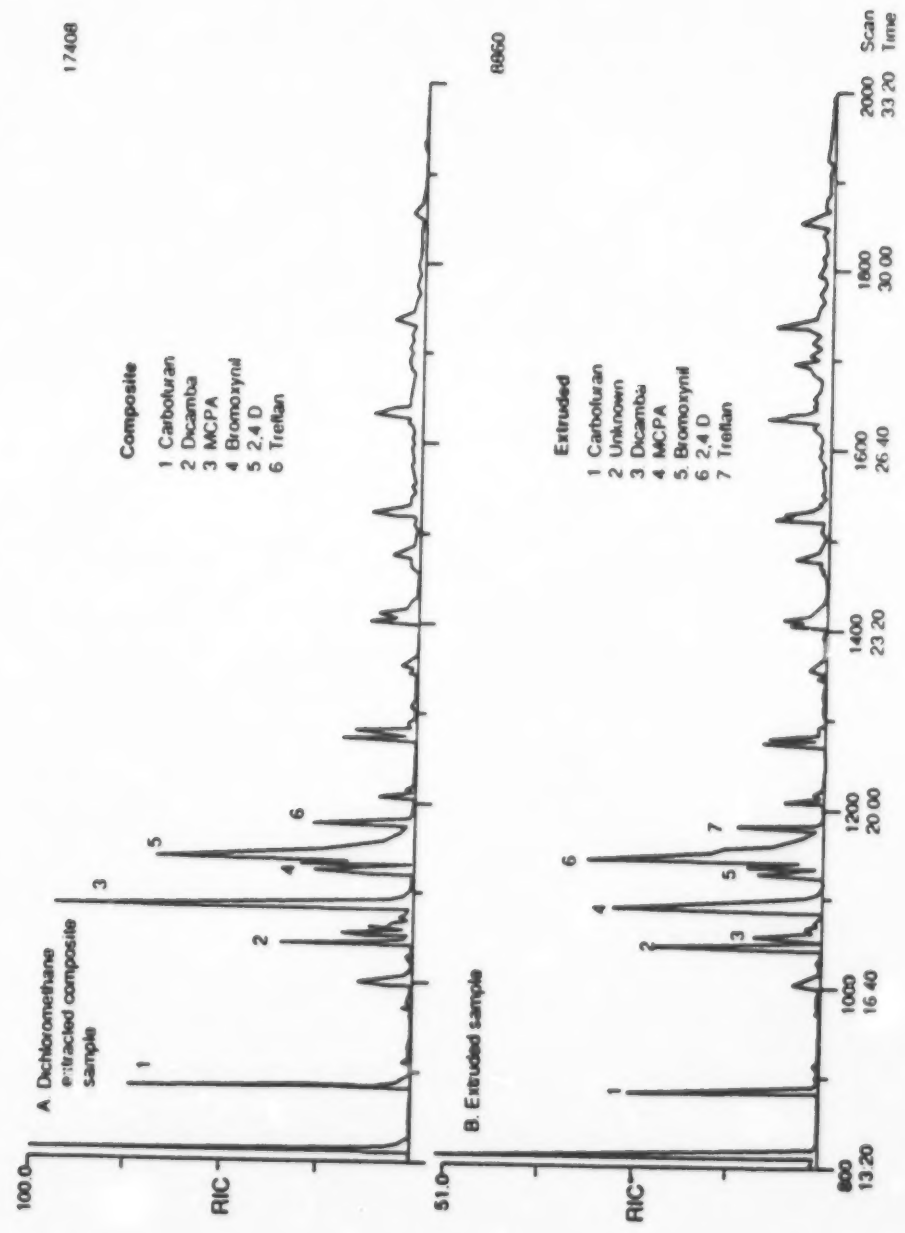


Figure 2. Pesticides found in composite mixture and extruded samples.

Table 2

Pesticides Found in the Plastic Samples

1. Carbofuran Furadan (FMC)	2,3-dihydro-2, 2-dimethyl-7-benzofuranyl methylcarbamate
2. Eptam (EPTC) Eptam (STAUFFER)	S-ethyl dipropylthiocarbamate GENEP EPTC (PPG)
3. Dicamba Banvel (Velsicol)	Dimethylamine salts of - 3,6-dichloro-o-anisic acid
4. MCP	Isooctyl ester of 2-methyl-4-chlorophenoxy-acetic acid
5. MCPA	2-Butoxethyl ester of 2-methyl-4-chlorophenoxy-acetic acid
6. 2,4-D	2,4-Dichlorophenoxyacetic acid
7. Unknown	Contains chlorine
8. 2,4-DB	4-(2,4-dichlorophenoxy) butyric acid (dimethylamine salt)
9. Treflan Treflan (Elanco)	Trifluralin- (a,a,a,-trifluoro-2,6-dinitro-N, N-dipropyl-p-toluidine)
10. Bromoxynil Buctril (Rhone-Poulenc)	3,5-dibromo-4-hydroxybenzonitrile (octanoic acid ester)
11. Unknown	Containing nitrogen and sulfur ring system
12. Unknowns	Many in low concentrations--altered residues?

3. PESTICIDE REMOVAL TRIALS

One of the stated objectives of the study was to identify a possible method of removing pesticides from the shredded plastic containers. It was hoped that a simple method might be found to reduce the concentration of the pesticides contained in the bulk plastic so that they would not be, or be perceived, as a health or environmental hazard in the products manufactured.

The following three methods were considered:

- Washing the plastic with readily available liquids;
- Volatilizing the pesticides with hot gases;
- Diluting of the plastic with virgin resin.

The first and second methods were investigated further.

3.1 Solvent and Water Washing

Simple agitation of the plastic in various hot solutions was tried and three different solvents were used. The first chosen was water and detergent, but because of the potential expense of disposal of the contaminated water and detergent, and the low level of pesticide made soluble using this solution, two other solvents were also tried (methanol and dichloromethane).

3.1.1 Washing Test Procedure

As discussed above, three solvents were used to extract the samples:

- 1) water plus 1% detergent;
- 2) methanol; and
- 3) dichloromethane

In each of the three trials a 3-litre portion of the composite sample was washed successively with 1-litre portions of solvent.

Figure 3 shows the array of pesticides that were detected in the methanol-wash solution from the GC-MS analysis in each sequential 1 litre wash, using methanol as the solvent. The data show a decrease in the concentration of pesticides found in the sequential washes.

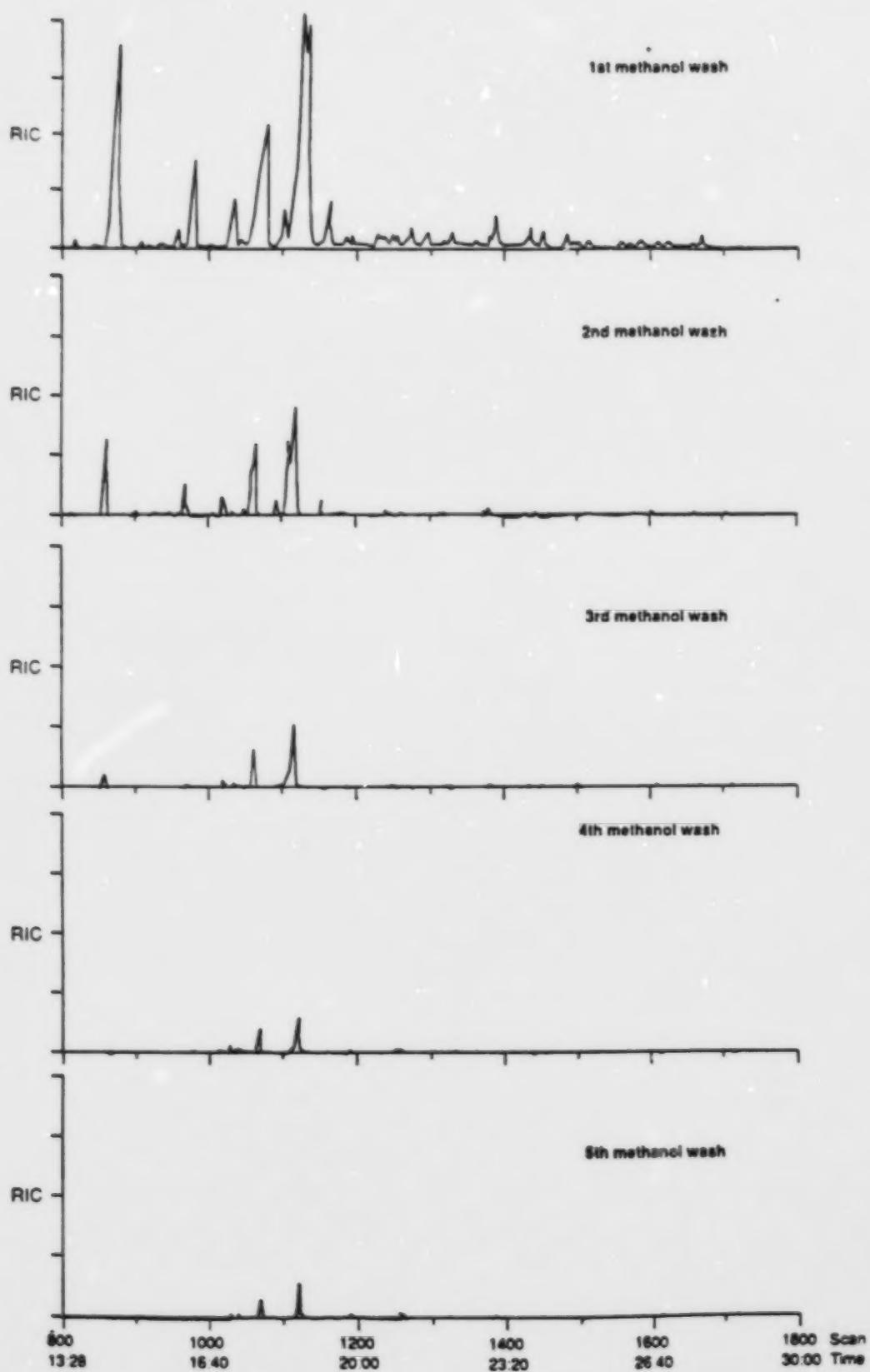


Figure 3. Pesticides present in methanol wash.

Figure 4 shows the results of the GC-MS analysis for the first and last sequential washing from the dichloromethane washing test.

The water/detergent extracts were not analyzed directly because of experimental difficulties in analyzing aqueous solutions. Instead, a small portion of each of the three washed composite samples were extracted individually with dichloromethane soxhlet extraction for three hours. The results of a GC-MS analysis of the pesticides extracted from the composite samples washed in the water/detergent solution is presented in Figure 5. All three composite samples washed in the three different solutions reveal the presence of at least some extractable pesticides.

3.1.2 Extruding of Washed Pesticide Plastic

The washed materials were extruded separately through a one-inch extruder. The extruded material was then pulverized and the respective samples extracted for at least three hours with dichloromethane in a soxhlet extractor. The chromatograms of the dichloromethane extract from the washed materials is presented in Figure 6. All samples showed the presence of pesticides.

3.2 Volatilization by Hot Gases

A sample of the composite mixture of washed plastic was placed in a glass vessel fitted with a nitrogen gas inlet. The vessel was then heated in a sand bath over which hot nitrogen gas was passed. Several trials were run at various temperatures, and for various lengths of time.

At 130° C approximately 6% of the extractable material was volatilized after one hour. the remainder of the pesticides present in the original material was readily extractable with dichloromethane.

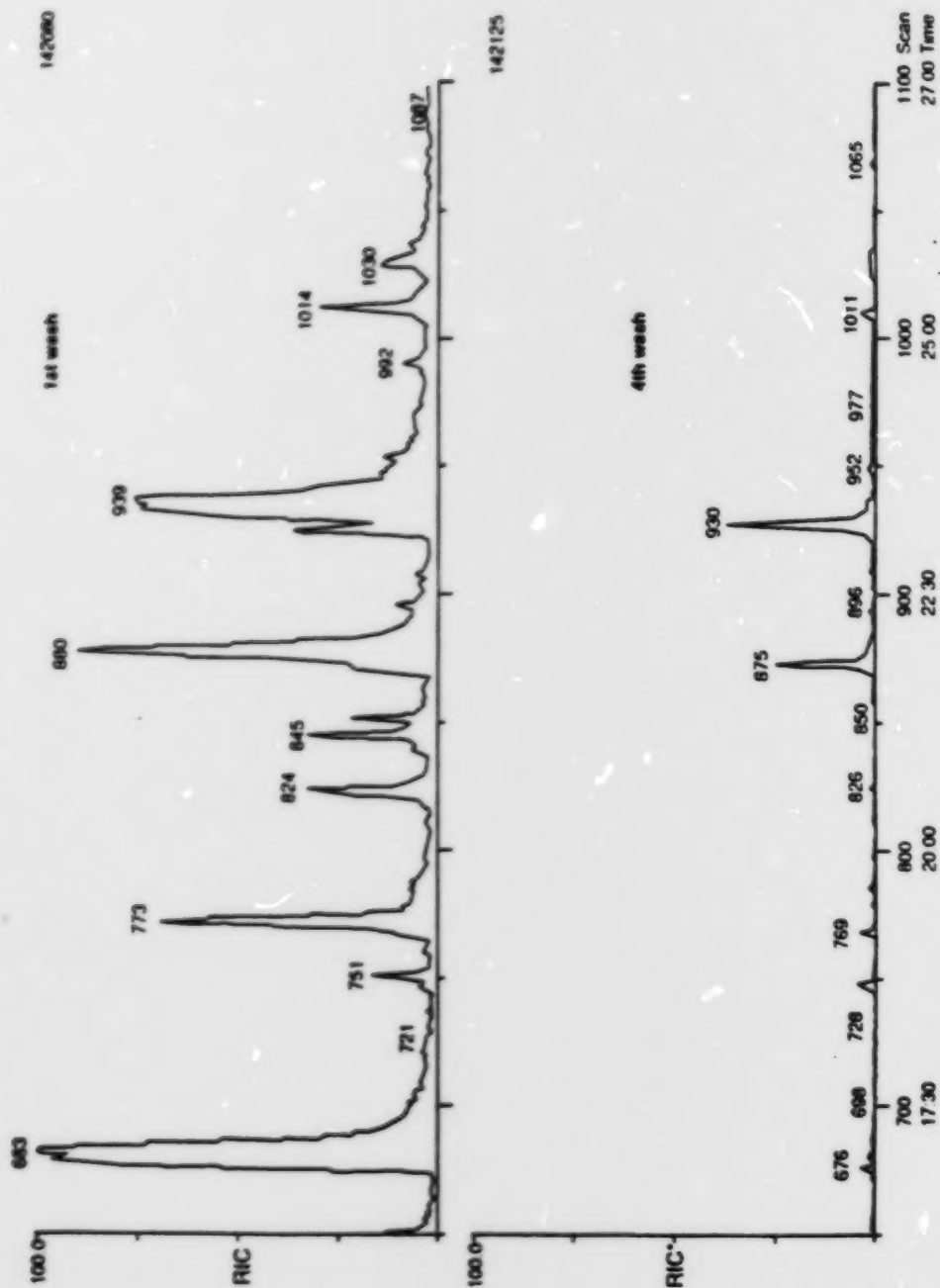


Figure 4. Pesticides present in dichloromethane washing.

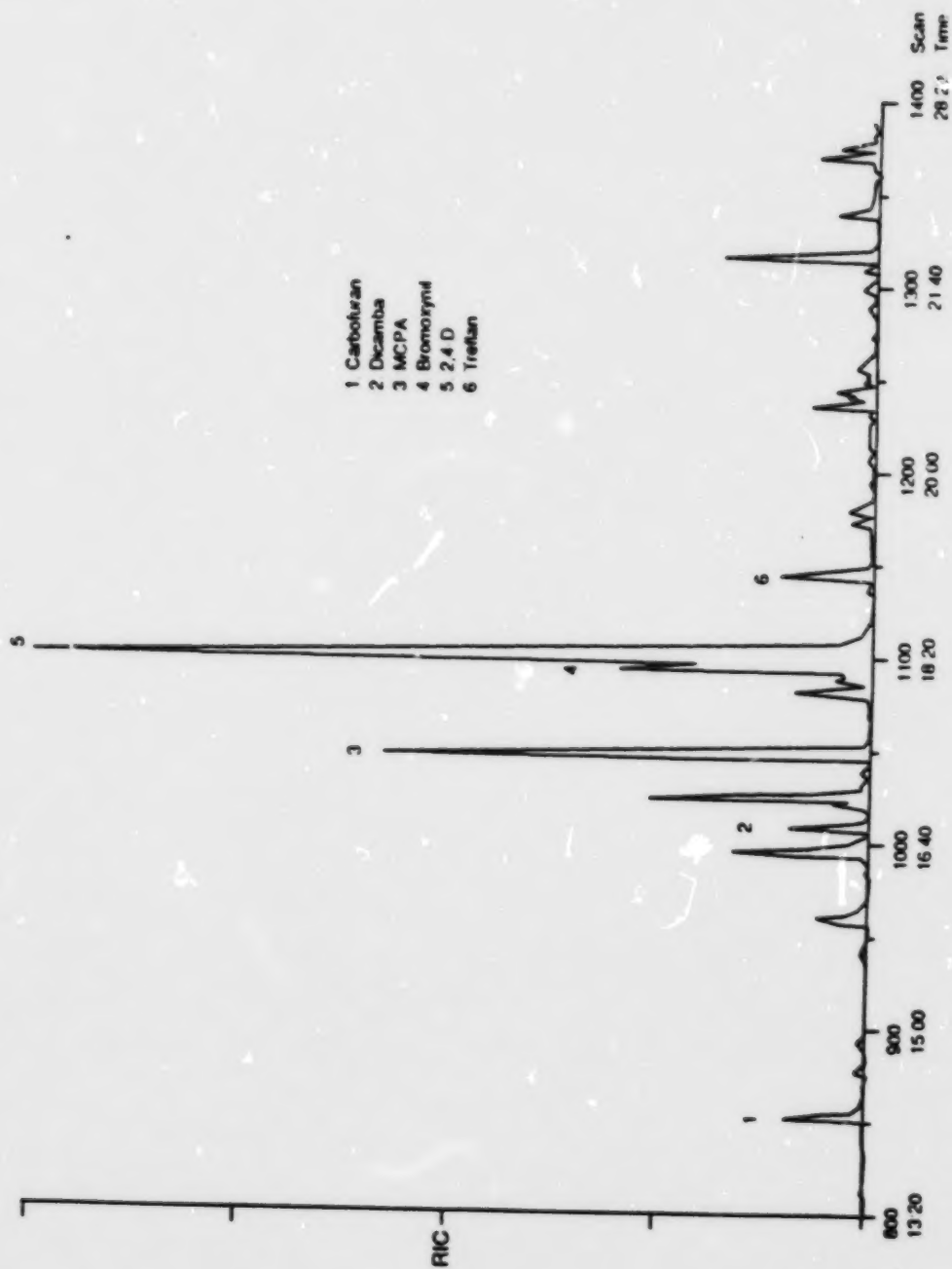


Figure 5. Extractable pesticides after washing water and detergent

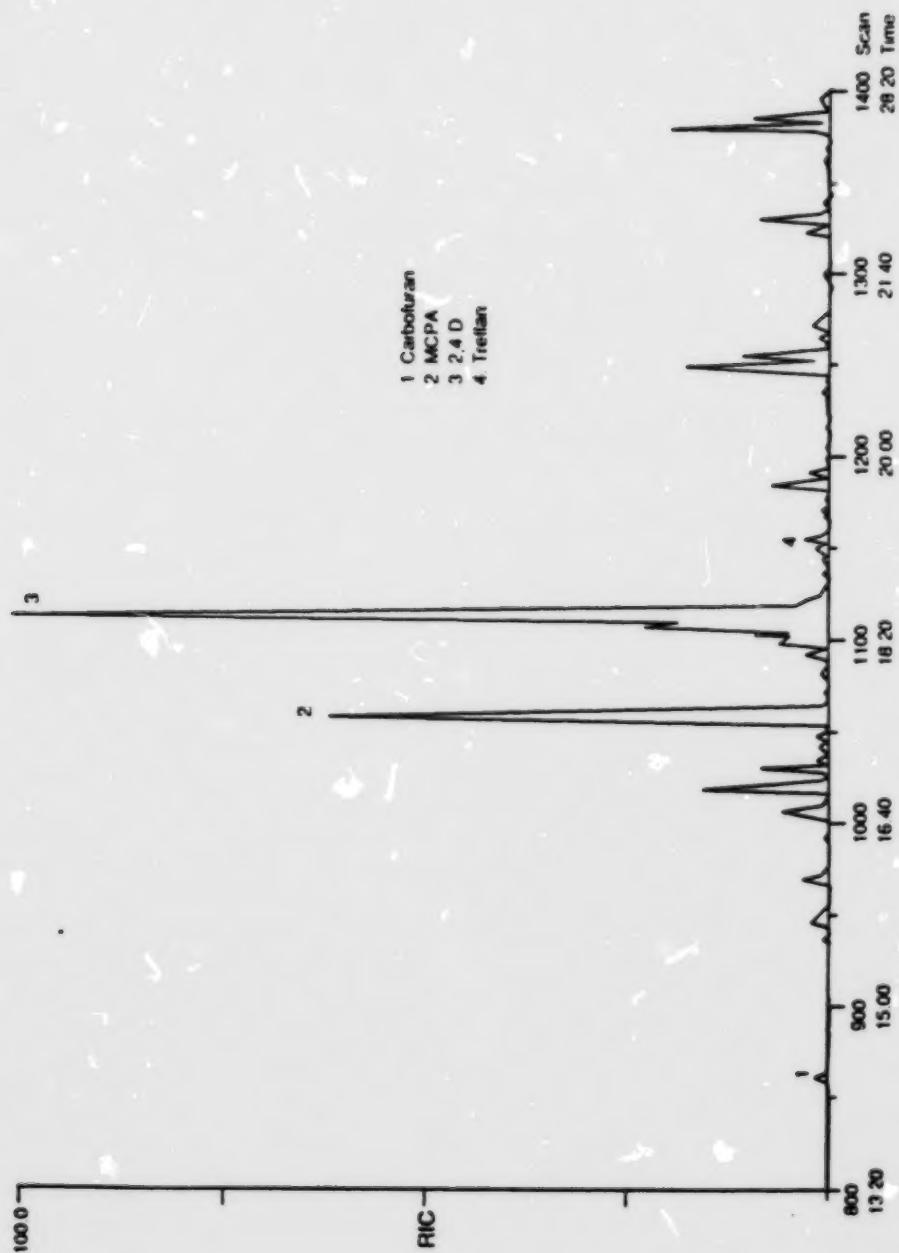


Figure 6a. Dichloromethane extraction of dichloromethane washed, extruded, pulverized plastic

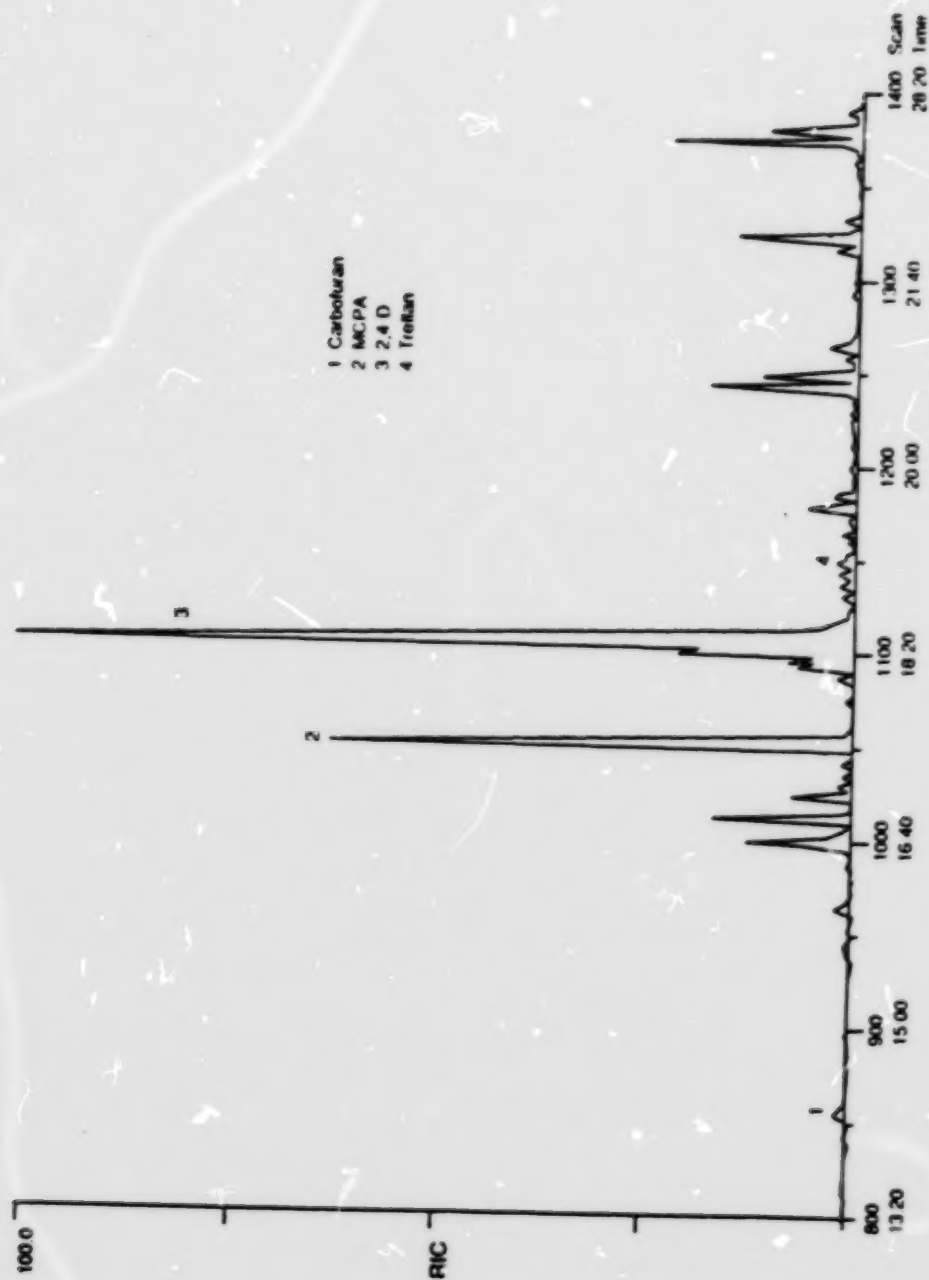


Figure 6b. Dichloromethane extraction of methanol-washed, extruded, pulverized plastic

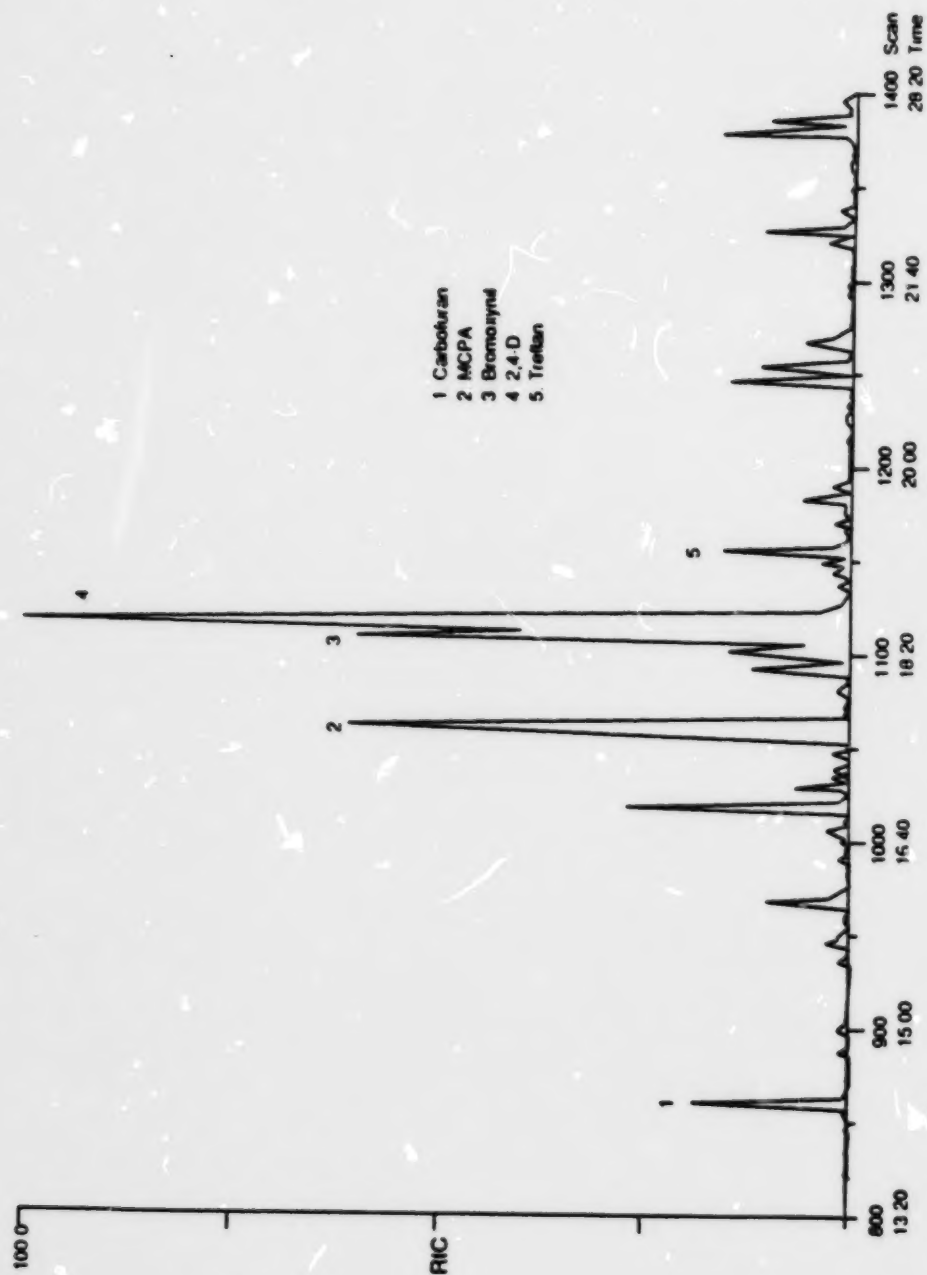


Figure 6c. Dichloromethane extraction of water-washed, extruded, pulverized plastic.

At 200° C about 30% of the material was volatilized after one hour, with the original pesticides easily extractable from the heat-treated plastic. The relative concentrations of the different types of pesticides found in the volatile material changed with temperature; however, most of the same types of pesticides were observed in both the volatilized plastic and in the extract of the residual. A few additional peaks in the chromatograms are attributable to decomposition products of the original pesticides.

4. OTHER TYPES OF ANALYSES PERFORMED

4.1 Solids Probe - Pyrolysis Mass Spectroscopy Analysis

Small portions of various samples of the original shredded plastics were analyzed directly using a solids probe on the mass spectrometer. This method allows the volatile products to be measured as the sample is heated directly in the mass spectrometer inlet.

In all but one of the samples, the pesticides treflan and bromoxynil were detected. The exception was the sample that had been washed in methanol five consecutive times, then extruded, pulverized and extracted using dichloromethane. Figure 7 shows the solids probe mass spectrum of this sample. Figure 8 shows the solids probe mass spectrum of the residual pesticides present in the dichloromethane-washed/extruded/ pulverized/dichloromethane extracted plastic.

The lines shown at $m/z = 335$ and 196 of the Figure 8 mass spectrum are characteristic of the pesticides Treflan and Bromoxynil respectively. The absence of these peaks in the spectra shown in Figure 7 indicates that the concentration of these pesticides in the plastic was below the detection limit of this technique. Our best estimate of the detection limit concentration of these two particular pesticides is one to ten ppm.

A Treflan container previously supplied by Alberta Environment was divided into sections; the sectioned plastic was then split into an inner, a center, and an outer portion. The inner portion was a slice taken from the inside of the container exposed to the solution. The outer portion was a thin slice of plastic taken from the outside of the container. The middle portion was a thin slice removed from the inner part of the plastic wall. These samples were then analyzed by solids probe MS.

The results indicated that in the neck joint of the container Treflan was present throughout the plastic, being detected on all three thin sectioned portions. The sample taken from the bottom of the container suggested that there may be less Treflan pesticide on the outer portion of the sample than in the middle and inner portions of the plastic wall; however, the presence of Treflan was detected throughout the wall thickness.

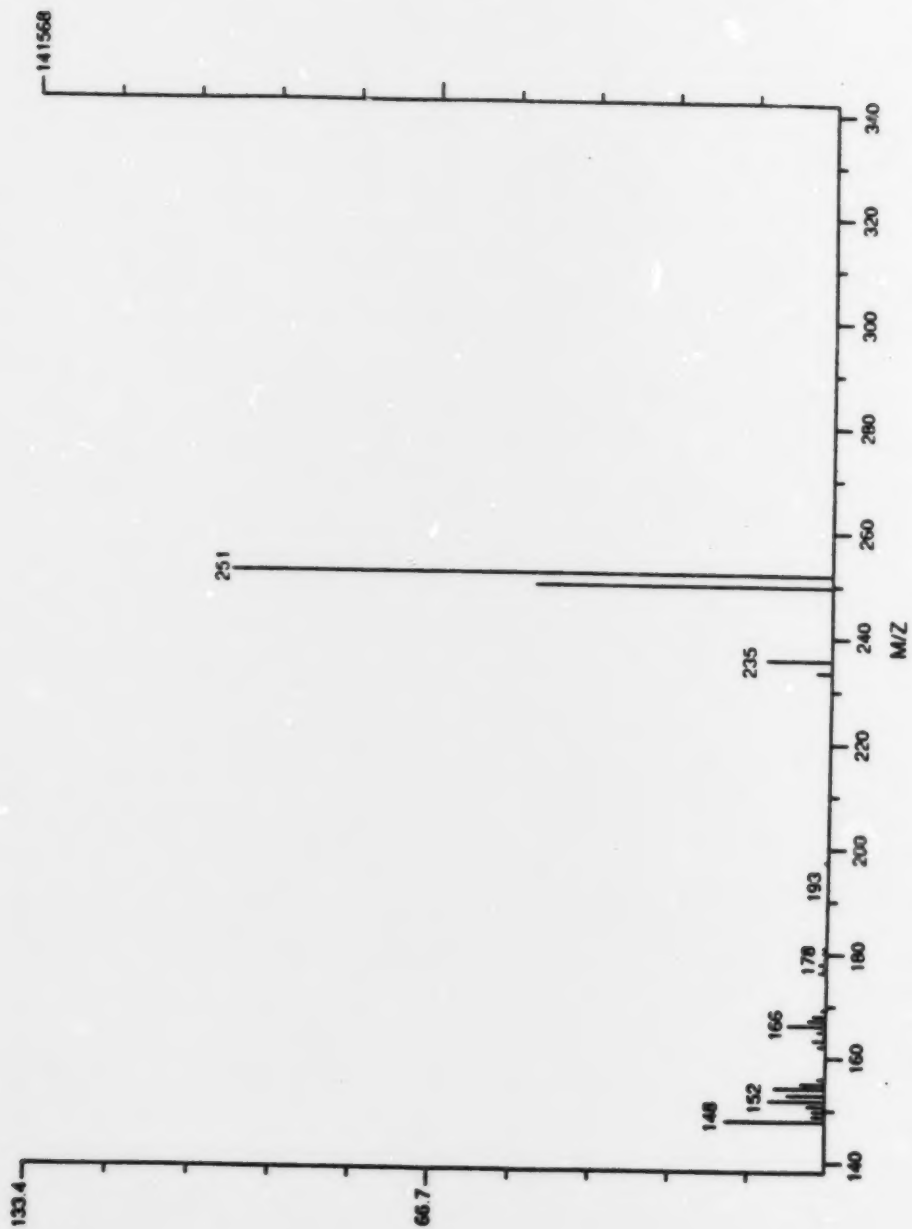


Figure 7. Solids probe analysis of methanol washed, extruded, pulverized, dichloromethane-extracted plastic.
(Signal intensity normalized to largest peak on Figure 8 vs. mass/charge ratio.)

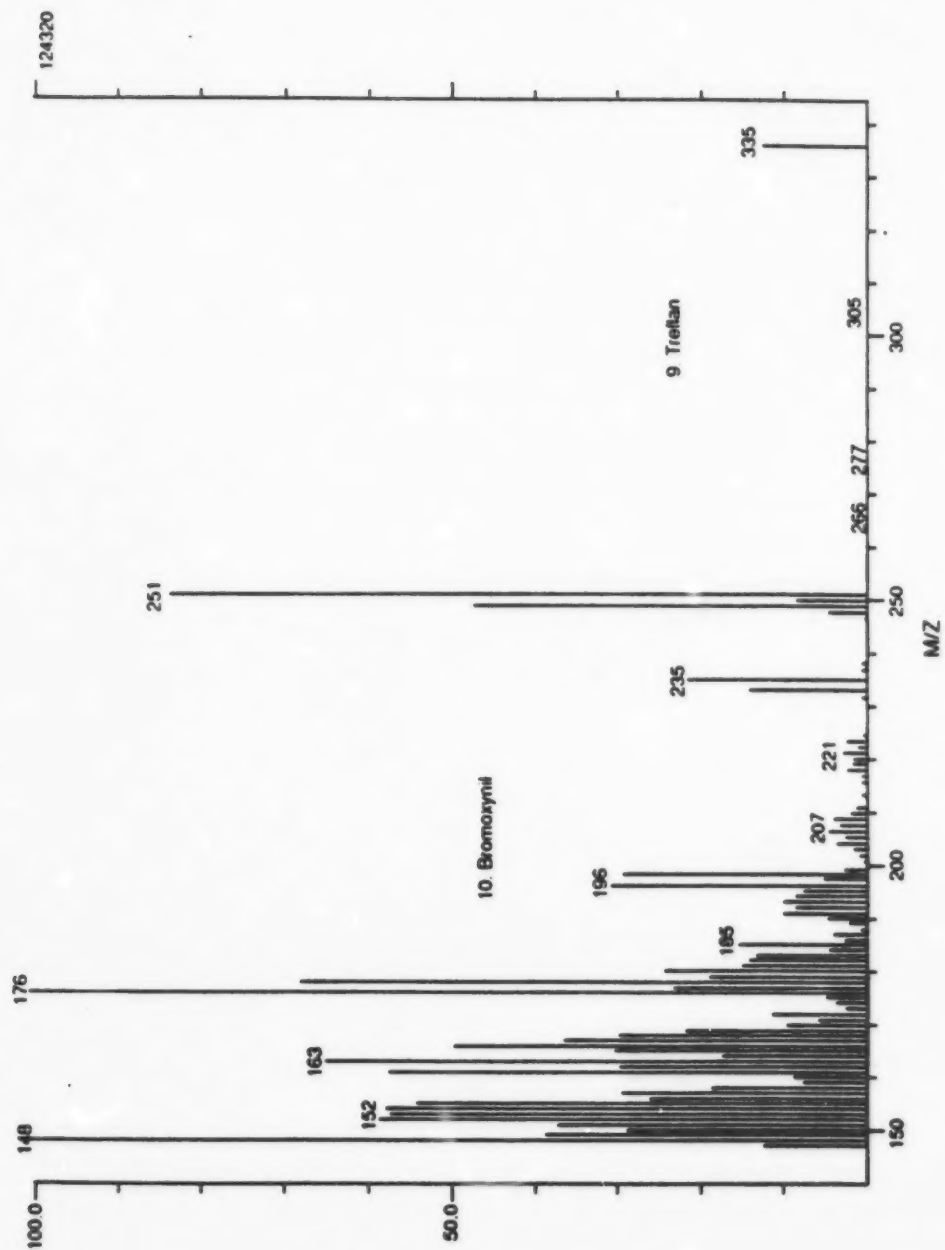


Figure 9. Solids probe analysis of dichloromethane-washed, extruded, pulverized, dichloromethane-extracted plastic

4.2 Plastic Analysis by Fourier Transform Infrared Spectroscopy (FTIR)

The composite sample consisted of various colored particles of shredded plastic and pieces of thin film. Samples of each of the colored particles and thin films were physically separated and analyzed by FTIR to determine their composition. The results are shown in Table 3. The majority of the samples were polyethylene or polyethylene copolymers. The "blue" particles were polypropylene.

The ash content of the most common colored particles varied from 0.2 to 1.1270. X-ray fluorescence analysis indicated that the ash consisted of titanium, silica and calcium. The results for these analyses are presented in Appendix B.

Table 3

Chopped Mixed Polymers

COLOR	TYPE OF POLYMER
Orange	Polyethylene
Yellow	Polyethylene
Blue	Polypropylene
Grey	Polyethylene
Black	"
Red	"
Pink	"
Translucent-Creamy	"
Translucent-Pink	"
White (pink tone)	Polyethylene/nylon
White (yellow tone)	Polyethylene
White (blue tone)	"
Thin film (white)	Polyethylenepolyvinylacetate
Thin film (red)	Polyethylene
Thin film (green)	"
Thin film (varied)	Polyethylene/polyvinylacetate
Thin film (peach)	polyethylene

5. PRESENTATION OF PRELIMINARY RESULTS TO INDUSTRY

Rather than try and derive a list of possible products internally, it was decided that the best course of action was to present the preliminary results of the chemical and material evaluation done by the Alberta Research Council, to an audience of potential industrial users of recycled plastic. Also, information regarding the Alberta Research Council's Joint Research Venture program was provided. Using this program, interested applicants could obtain 50% of the funds for product development.

A list of those present at the meeting appears below:

Representative	Company	Phone/Fax#
Bertram, B.	Alberta Research Council	450 5407
Berzins, B.	Newalta Environmental Services	450 5477(FAX) 266 6556 265 9034(FAX)
Bohdan, B.	Technology, Research & Telecommunications	422 0567 420 1474 (FAX)
Boyd, W.	Alberta Environment	427 5855
Briggs, R.	Glen Lynn Engineering Ltd. (Representation A.S.W.M.C.)	487 3153
Byrtus, G.	Alberta Environment	427 5855
Campbell, S.	Agritrends Research Inc.	320 1688
Collison, S.	Problem Waste Management	948 3449 948 3338(FAX)
Cunningham, B.	Promold Marketing Inc.	939 2523
Cunningham, E.	Promold Marketing Inc.	939 2523
Elson, J.	Squires Enterprises Group Inc. (Calgary)	269 3141 263 0100(FAX)
Galbraith, G.	Crop Protection Institute of Canada	483 7971 489 6445(FAX)
Heidrick, T.	Alberta Research Council	450 5401 450 4577 (FAX)
Macinnis, T.	Alberta Recoveries/Rentals Ltd.	527-7003
Makwich, R.	Provincial Plastics	962 9400 962 4900(FAX)
Ronden, C.D	Ronden & Associates Ltd.	437 5554 436 5214(FAX)
Sutton, S.	Alberta Special Waste Services Association	467 3233
Van Teeling, C.	Alberta Environment	427 5855

In this way, the most practical products would be developed. As a result, two requests for further information were received, and at present one joint research venture proposal is being prepared for use of the pesticide plastic containers. This will be submitted to the Alberta Research Council for approval in the standard manner.

6. CONCLUSIONS

1. All washing techniques reduced pesticide levels in the plastic. The solvent washes removed more than detergent and waster washes, with dichloromethane being the most effective solvent tried.
2. Bromoxynil and Treflan are two pesticides that may be dissolved into the plastic. These pesticides in particular were very difficult to remove by washing or by solvent extraction.
3. For one small test sample that was washed five times with methanol and then extruded, it was possible to lower the level of the Bromoxynil and Treflan in the plastic to less than the detection limit of the system (~1 to 10 ppm) utilizing a subsequent dimethylchloride wash. To determine whether this is possible for larger samples (or the bulk plastic) or if the concentration could be lowered further, would require extensive further work.
4. The concentration of pesticides may be reduced in the recycled plastic by judicious sorting of the containers before homogenizing the sample. This selective collection would reduce the chances of contaminated and the more hazardous materials being present in the recycled material. (Carbofuran was observed in most of the samples in the study).
5. Acceptable concentrations of pesticide in plastics used for recycling and in the products made from the plastic must be established. Methods of quantifying the acceptable concentrations of each of the pesticides that may be present in the recycled plastic have to be established.
6. Although the plastics used in the containers may be amenable to producing recycled products, there may be potential hazards to workers associated with the residual pesticide during the manufacturing stages.
7. Even though the plastic may have low intrinsic value, since it is weathered and mixed and therefore has variable physical properties, there has been sufficient interest from the industry contacted to start developing one Joint Research Venture proposal for product development.

APPENDIX A

GC/MS METHOD FOR ANALYSIS OF PESTICIDE EXTRACTS

Extracts from the plastics were diluted to 100 ml with dichloromethane. 100 μ l of this solution was added to a reaction vial. 100 μ l of 0.2N methanolic (m-trifluoromethylphenyl) trimethylammonium hydroxide was added to the vial. The solution was shaken vigorously and left to stand for 20 minutes.

2 μ l of the solution was injected onto a Supelco SPB-1 fused silica column, 20 meters long, 0.25 mm ID, 0.25 μ m df. Gas chromatogram conditions were 65°C for 5 minutes then 10°C/minute to 295°C. A Finnigan-Mat 4500 mass spectrometer was used to detect and identify pesticides as they eluted from the gas chromatogram.

The above method derivatizes carbofuran, phenoxy herbicides (e.g. 2,4-D, MCPA) and benzoic herbicides (e.g. Dicamba) to more compounds which are easier to identify by GC/MS.

APPENDIX B

SOLID PROBE MASS SPECTROMETER METHOD FOR DETECTION OF TREFLAN AND BROMOXYNIL RESIDUES IN PLASTIC

A micro vial containing barely visible particle of plastic (less than 100 mg) was put in the mass spectrometer solid probe. The solid probe was heated at 50° C/minute to 280° C, distilling volatiles into the mass spectrometer.

The mass spectrometer was operated using oxygen chemical ionization, negative ion detection in a full scan mode to minimize interferences and maximize detection for Treflan and Bromoxynil.